funnel charged with 1.42 g (0.02 mole) of isobutyraldehyde, 1.0 mL of H_2O, and enough CH_3OH to bring the total volume to 5 mL were placed 0.16 g of potassium hydroxide, 1.0 mL of CH_3OH, and 2.42 g (0.02 mol) of 4,4-dimethylcyclohex-2-enone (1). The contents of the dropping funnel were discharged dropwise over a period of about 20 min. The reaction mixture was stirred at room temperature for 2 h and then processed by diluting with 50 mL of H_2O and extracting with ether (4 × 50 mL). The combined extracts were dried ($MgSO_4$) and concentrated under vacuum to give 3.4 g of pale yellow liquid which was shown (by comparison of spectra obtained with samples isolated by preparative gas chromatography) to consist of ketones **2**, **3**, and **4** in the approximate ratios of 1.5:1.0:3.2, respectively, in addition to starting materials.

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Stereochemical Studies with 1,2,5-Trimethyl-1-silacyclopentanes

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Chlorination of 1,2,5-trimethyl-1-silacyclopentane by benzoyl peroxide/carbon tetrachloride proceeds with 100% retention of configuration at silicon, but reaction with triphenylmethyl chloride in benzene gives two-thirds retention and one-third inversion. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane isomerizes slowly in nonpolar solvents, but salts strongly enhance the rate of isomerization. Displacement of chloride by fluoride and by methoxide is nonstereospecific but, in the case of the latter, is stereoselective. Displacement of chloride by acetate proceeds with predominant inversion of configuration at silicon. The kinetics of the isomerization of 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane by methoxide have been studied.

The 1,2,5-trimethyl-1-silacyclopentane system is an excellent substrate to study the stereochemical course of reactions in which silicon is involved. Assignment of configuration of its *Z,Z* and *E,E* isomers can be made with confidence by determination of the chemical shifts of silicon methyls in the proton and ^{13}C NMR spectra and comparison of these values with those of the *E,Z/Z,E* isomer, which can be identified unambiguously.[1]

1-Chloro-1,2,5-trimethyl-1-silacyclopentane. Conversion of 1,2,5-trimethyl-1-silacyclopentane into the chloride by hydrogen–halogen exchange with triphenylmethyl chloride in benzene proceeded smoothly but nonstereospecifically. Thus a mixture of (*E,E*)- and (*E,Z/Z,E*)-1,2,5-trimethyl-1-silacyclopentanes was converted into a mixture consisting of all three 1-chloro-1,2,5-trimethyl-1-silacyclopentanes with the *E,Z/Z,E* content unchanged but now having *Z,Z*:*E,E* ≈ 2:1. This is not the equilibrium distribution for the *Z,Z* and *E,E* isomers as determined by isomerization studies described below. It is clear that the simple S_Ni-Si mechanism postulated for this exchange reaction in benzene on the basis of retention stereochemistry[2] must be revised in the light of this finding of two-thirds retention and one-third inversion. S_Ni-Si and S_N2-Si mechanisms may be operative competitively. Alternatively, the silicon–hydrogen bond may be broken before the silicon–chloride bond is formed, thus allowing attack from either side of the silicenium ion pair. Similar results were reported for acyclic asymmetric silicon compounds.[3]

The reaction between 1,2,5-trimethyl-1-silacyclopentane and carbon tetrachloride, initiated by thermal decomposition of benzoyl peroxide, proceeded stereospecifically. Thus, a mixture of isomers with *E,E*:*E,Z/Z,E*:*Z,Z* = 2:2:96 was converted into a mixture of chlorides with a ratio of 2:2:96 and a mixture with *E,E*:*E,Z/Z,E*:*Z,Z* = 57:43:0 into a chloride mixture with a 57:43:0 ratio, within experimental error (±1).

The assignment of configuration of the chlorides was based on their proton and carbon NMR properties, which are given, together with those of the *E,Z/Z,E* isomer, in Tables I and II. The same arguments concerning mutual shielding and deshielding were used as for the corresponding hydrides.[1] Thus the *Z,Z* chloride, corresponding to the *E,E* hydride, has the least shielded silicon methyl in the proton and ^{13}C spectra while these are most shielded in the *E,E* isomer. The C-2 methyls are similarly affected although to smaller extent.

The CCl_4 reaction proceeds with retention of configuration at silicon, in agreement with analogous reports for 1,2-dimethyl-1-silacyclobutane[4] and 1,2-dimethyl-1-silacyclopentane,[5] where retention stereochemistry was ascribed to the pyramidal structure of the silyl radical intermediate postulated for this reaction and the fact that there were no known examples of stereospecific inversion reactions at a radical center.

The *E,E* and *Z,Z* chlorides are configurationally stable in pure form but isomerize slowly in chloroform solutions in the course of a few days. In some cases however, due

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Table I. Proton Chemical Shifts of 1-Chloro-1,2,5-trimethyl-1-silacyclopentane[a]

	E,E[b]	E,Z/Z,E	Z,Z[c]
$SiCH_3$	0.405 (s)	0.412 (s)	0.471 (s)
CCH_3	1.02 (d, J = 7.52 Hz)	1.10 (d, J = 7.08 Hz) 1.06 (d, J = 7.30 Hz)	1.15 (d, J = 7.08 Hz)

[a] In ppm, relative to Me_4Si, at 270 MHz. [b] Corresponding to Z,Z hydride. [c] Corresponding to E,E hydride.

Table II. ^{13}C Chemical Shifts of 1-Chloro-1,2,5-trimethyl-1-silacyclopentanes[a]

	E,E	E,Z/Z,E	Z,Z
$SiCH_3$	−4.03	−1.92	0.71
CCH_3	14.87	14.34, 14.64	15.22
C_2, C_5	22.53	22.65, 23.94	21.25
C_3, C_4	33.01	34.06, 34.23	33.10

[a] In ppm, relative to Me_4Si, at 67.89 MHz.

to impurities of unknown composition, almost complete isomerization was observed within a few hours, even when stored without solvent at −12 °C. To investigate the nature of these impurities and the way in which conversion occurred, we followed the isomerization of (E,E)-1-chloro-1,2,5-trimethyl-1-silacyclopentane in solution using varying concentrations of salt. Tetra-n-butylammonium iodide, which is soluble in organic solvents and would be expected not to react with the substrate to form the corresponding iodide,[6] was used. The isomerization in CS_2 solution followed first-order kinetics with respect to both isomers with a logarithmic time dependence of concentrations according to

$$E,E \underset{k'}{\overset{k}{\rightleftharpoons}} Z,Z$$

$$-\mathrm{d}[E,E]/\mathrm{d}t = k[E,E] - k'[Z,Z]$$

$$\ln\left(\frac{[E,E]_0 + [Z,Z]_0 - [E,E]_e}{[E,E]_t - [E,E]_e}\right) = (k + k')t$$

From an initial mixture of isomers of E,E:E,Z/Z,E:Z,Z = 80:2:18, the equilibrium, E,E:E,Z/Z,E:Z,Z = 44:2:54, was established in 10 min (approximately equimolar amounts of substrate and iodide) to ~6 h (substrate–iodide = 100:1). The equilibrium concentrations did not vary with the amount of catalyst used. Individual rate constants are given in the Experimental Section. These rate constants depend in a linear way on the concentration of tetra-n-butylammonium iodide and correspond to second-order rate constants of (7.3 ± 0.2) × 10^{-2} M^{-1} s^{-1} for E,E → Z,Z and (6.0 ± 0.2) × 10^{-2} M^{-1} s^{-1} for Z,Z → E,E and hence an equilibrium constant of 1.2 ± 0.1 in favor of the Z,Z isomer. An uncatalyzed rate of ca. 3 × 10^{-5} s^{-1} is also indicated.[7] This suggests a salt-supported formation of a silicenium ion intermediate in the rate-determining step, followed by attack of chloride from either side of an almost planar intermediate.

It is not surprising that the Z,Z isomer with its silicon methyl group in a trans position to the carbon methyl groups is slightly enriched in the equilibrium mixture. The van der Waals radius of the methyl group is 2.0 Å compared to 1.8 Å for chloride.[8] Salt-induced racemization of optically active α-naphthylphenylmethylchlorosilane has been observed and similarly explained by the S_N1-Si mechanism,[9a] although a preferred alternative explanation has been offered.[9b]

A complex mixture of products formed when 1,2,5-trimethyl-1-silacyclopentane was treated with an equimolar amount of bromine, and this reaction was not further investigated.

1-Methoxy-1,2,5-trimethyl-1-silacyclopentane. The reaction of 1-chloro-1,2,5-trimethyl-1-silacyclopentane with sodium methoxide, complete within a few minutes, proceeds stereoselectively. Thus, when the mixture of chlorides Z,Z:E,Z/Z,E:E,E = 32:45:23 was used, a 5:45:50 mixture of methoxides was formed. Similarly a Z,Z:EE = 55:45 mixture of chlorides gave essentially only one product. The major isomer, on the basis of its shielded silicon methyl resonance in proton and carbon spectra—with respect to the E,Z/Z,E isomer and the minor isomer (see Tables III and IV)—was assigned the E,E structure. The carbon methyls cis to the silicon methyl are not the more shielded pair as is found in the case of the hydride and chloride above. Shielding by the methoxy group exceeds that of the methyl group. This is also observed in the cases of the fluoride and the acetate below.

Stereoselectivity has also been reported in the reaction of 1-chloro-1,2-dimethyl-1-silacyclopentane with alcohols, but exclusive formation of the E isomer occurs only with sufficiently hindered reagents.[5]

1-Fluoro-1,2,5-trimethyl-1-silacyclopentane. This compound was obtained by the action of silver fluoride or tetra-n-butylammonium fluoride on the corresponding chloride. Boron trifluoride, which caused decomposition of the hydride, reacted only very slowly with 1-chloro-1,2,5-trimethyl-1-silacyclopentane.

The displacement of chloride by fluoride proceeds with a change in the configuration of silicon. This is not surprising, as the rate of isomerization of the chloride exceeds by far its rate of conversion to the fluoride. Thus, independent of the isomeric composition of the chloride at the start of the experiment, equilibrium between the E,E and Z,Z chloro isomers (45:55) was established after a short period (~1 h), while the conversion to the fluoride had proceeded only to a minor extent. It is interesting to note that after equilibrium between E,E and Z,Z isomers had been established, the concentration of the E,Z/Z,E isomer relative to the E,E and Z,Z isomers changed with time. This chloro compound was converted to the corresponding fluoro compound at a considerably faster rate, indicating lower steric hindrance in the course of the reaction. 1-Fluoro-1,2,5-trimethyl-1-silacyclopentane was formed in a ratio of Z,Z:E,E = 62:38 with an E,Z/Z,E content determined by the composition of the starting chloride. The reaction of 1-chloro-1,2-dimethyl-1-silacyclopentane with zinc fluoride is reported to be stereoselective as a result of rapid isomerization.[10]

Structure assignment was again based on observation of the silicon methyl groups. Proton NMR shifts for all three isomers are given in Table V and ^{13}C NMR shifts

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(7) These second-order rate constants correspond to k_0b values in the expression $k_{obsd} = k_0(1 + b[salt])$ for a linear salt effect on a first-order reaction having $k_0 \approx 3 \times 10^{-5}$ s^{-1}, i.e., $b \approx 2 \times 10^3$ M^{-1}.

(8) L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals", Cornell University Press, Ithaca, N.Y., 1948.

(9) L. H. Sommer, F. O. Stark, and K. W. Michael, J. Am. Chem. Soc., 86, 5683 (1964); (b) L. H. Sommer, G. D. Homer, A. W. Messing, J. L. Kutschinski, F. O. Stark, and K. W. Michel, ibid., 93, 2093 (1971).

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Table III. Proton Chemical Shifts of 1-Methoxy-1,2,5-trimethyl-1-silacyclopentanes[a]

	E,E	E,Z/Z,E	Z,Z
$SiCH_3$	0.122 (s)	0.126 (s)	0.139 (s)
CCH_3	0.98 (d, J = 5.75 Hz)	1.00 (d, $J \approx 8$ Hz) 1.09 (d, J = 7.30 Hz)	1.06 (d, J = 7.30 Hz)
OCH_3	3.43 (s)		3.52

[a] In ppm, relative to Me_4Si, at 270 MHz.

Table IV. ^{13}C Chemical Shifts of 1-Methoxy-1,2,5-trimethyl-1-silacyclopentanes[a]

	E,E	E,Z/Z,E	Z,Z
$SiCH_3$	−8.53	−6.43	−4.14
CCH_3	15.05	13.93, 14.87	14.28
C_2, C_5	17.80	19.20, 21.77	20.19
C_3, C_4	33.18	34.00, 21.77	31.48
OCH_3	50.21	50.67	50.97

[a] In ppm, relative to Me_4Si, at 25 MHz.

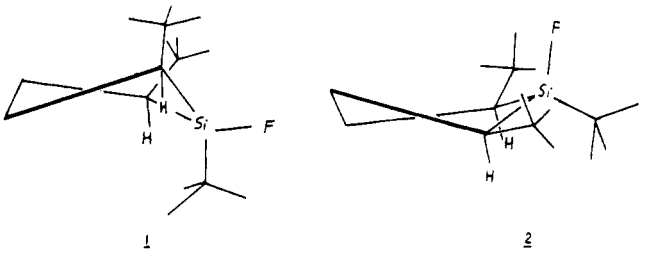


Figure 1. Conformers of (Z,Z)-1-fluoro-1,2,5-trimethyl-1-silacyclopentane. In 1 all methyl groups assume pseudoaxial positions. The dihedral angle between H-2 (H-5) and F is ~90°. In 2 all methyl groups lie close to the plane of the silacyclopentane ring, resulting in a dihedral angle between H-2 (H-5) of F of ~160°.

in Table VI. ^{19}F NMR provides a definitive supplement to the proton and ^{13}C NMR data. While the chemical shifts of the silicon methyl doublets are almost identical for the E,Z/Z,E and E,E isomers in the proton spectrum, the ^{19}F resonances are well separated: 98.4, 92.0, and 84.5 ppm upfield of trifluoroacetic acid. The 92.0-ppm signal arises from the E,Z/Z,E isomer. The signal at 98.4 ppm, 6.4 ppm upfield of that for E,Z/Z,E, was assigned to the Z,Z isomer, in which fluorine is shielded by two methyl groups in cis position; the one at 84.5 ppm, 5.5 ppm downfield of the E,Z/Z,E resonance, was assigned to the E,E isomer. The resonance at 98.4 ppm, i.e., Z,Z, appears as a quartet (J = 7.9 Hz), in contrast to the unresolved signals at 84.5 and 92.0 ppm, where coupling in addition to ^{19}F–Si–CH_3, namely, to H-2 and H-5, obscures the spectrum. This suggests that the predominant conformation of the Z,Z isomer is as shown in Figure 1. It is difficult to rationalize differences in the coupling constants ^{19}F–H-2-(H-5) between E,E and Z,Z isomers, in particular its being very small for Z,Z, unless a conformation for the latter is considered in which all methyl groups occupy pseudoaxial positions, with the dihedral angle between F and H-2(5) being approximately 90°.

1-Acetoxy-1,2,5-trimethyl-1-silacyclopentane. The isomers of 1-chloro-1,2,5-trimethyl-1-silacyclopentane were converted into the corresponding acetates by silver acetate at considerably different rates. Thus, a mixture of isomers originally containing Z,Z:E,Z/Z,E:E,E = 31:47:22 changed its composition to 29:45:27 after 1 h and to 18:35:47 after 5 h. The relative reactivities are thus Z,Z > E,Z/Z,E > E,E. After 24 h a small quantity of unreacted E,E remained, while the Z,Z and E,Z/Z,E isomers had disappeared completely. The first-order rates for reaction of the (E,Z/Z,E)- and (Z,Z)-1-chloro-1,2,5-trimethyl-1-silacyclopentanes are similar (9.0×10^{-5} and 9.7×10^{-5} s^{-1}, respectively), in contrast to the smaller rate constant for the E,E isomer (4.5×10^{-5} s^{-1}). This may reflect the difference in steric hindrance experienced by the approaching nucleophile due to the carbon methyl groups. The isomeric composition of the resulting acetates was found to be 20:47:33, indicating a high degree of stereospecificity.

1-Acetoxy-1,2,5-trimethyl-1-silacyclopentane is thermally unstable. Distillation at 60 mm led to extensive decomposition. When a sample was heated in the mass spectrometer inlet system, neither the molecular ion nor fragments thereof were detected. Instead, the mass of the molecular ion peak as well as the fragmentation pattern showed clearly the formation of bis[1-(1,2,5-trimethyl-1-silacyclopentyl)] ether in the ion source.

When a mixture of chlorides consisting predominantly of the E,E isomer (Z,Z:E,Z/Z,E:E,E = 9:3:88) was reacted with silver acetate, a mixture of acetates in the ratio A:B:C = 79:3:18 was obtained. Similarly, a mixture enriched in the Z,Z isomer (Z,Z:E,Z/Z,E:E,E = 76:23:2) yielded an acetate ratio of A:B:C = 10:23:67.

Proton and ^{13}C NMR shifts for compounds A and C are given in Tables VII and VIII, together with those of com-

Table V. Proton Chemical Shifts of 1-Fluoro-1,2,5-trimethyl-1-silacyclopentanes[a]

	Z,Z	E,Z/Z,E	E,E
$SiCH_3$	0.27 (d, J = 8.0 Hz[b])	0.22 (d, J = 8.0 Hz[b])	0.23 (d, J = 8.0 Hz[b])
CCH_3	0.99 (d, J = 5.7 Hz)	1.06; 1.02[c]	1.04 (d, J = 6.3 Hz)

[a] In ppm, relative to Me_4Si, at 100 MHz. [b] ^1H–^{19}F coupling. [c] Coupling constants could not be determined with accuracy due to overlapping signals.

Table VI. ^{13}C Chemical Shifts of 1-Fluoro-1,2,5-trimethyl-1-silacyclopentanes[a,b]

	Z,Z	E,Z/Z,E	E,E
$SiCH_3$	−2.83 (d, J = 15.6 Hz)	−5.41 (d, J = 15.0 Hz)	−7.09 (d, J = 15.3 Hz)
CCH_3	13.68 (d, J = 1.8 Hz)	13.10 (s) 14.26 (d, J = 2.2 Hz)	14.59 (d, J = 2.8 Hz)
C_2, C_5	19.64 (d, J = 13.1 Hz)	20.78 (d, J = 13.9 Hz) 20.14 (d, J = 12.5 Hz)	18.91 (d, J = 12.8 Hz)
C_3, C_4	32.68 (s)	33.72 (s) 33.50 (d, J = 4.4 Hz)	32.85 (d, J = 3.4 Hz)

[a] In ppm, relative to Me_4Si, at 25 MHz. [b] J arising from ^{13}C–^{19}F coupling.

Table VII. Proton Chemical Shifts of 1-Acetoxy-1,2,5-trimethyl-1-silacyclopentanes[a]

	A	B (*E,Z/Z,E*)	C
CH_3CO	1.99 (s)	2.05 (s)	2.02 (s)
$SiCH_3$	0.35 (s)	0.26 (s)	0.23 (s)
CCH_3	0.99[b] (d, J = 6.3 Hz)	1.05[b] (d, J = 6.8 Hz)	1.00[b] (d, J = 7.2 Hz)

[a] In ppm, relative to Me_4Si, at 100 MHz. [b] The carbon methyl groups appeared as broad singlets, sometimes accompanied by small satellites, and in B as a broad doublet. The values quoted were obtained from spectra run with different concentrations of shift reagent and extrapolated to zero concentration.

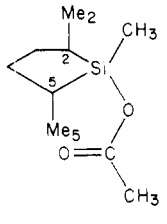
Table VIII. ^{13}C Chemical Shifts of 1-Acetoxy-1,2,5-trimethyl-1-silacyclopentanes[a]

	A	B (*E,Z/Z,E*)	C
$SiCH_3$	−2.54	−5.33	−7.63
CCH_3	14.23	14.71, 13.93	14.66
C_2, C_5	19.82	21.46, 20.68	18.78
C_3, C_4	32.74	34.25, 34.04	32.74

[a] In ppm, relative to Me_4Si, at 25 MHz.

pound B, which was obtained by converting (*E,Z/Z,E*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane to its acetoxy derivative. Important stereochemical information is accessible by the NMR spectra obtained in the presence of paramagnetic compounds. With its carbonyl group, 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane coordinates to the metal ion. While the carbon spectra are affected only to a minor extent and in an uninformative fashion, addition of the shift reagent $Eu(fod)_3$ led to proton spectra in which the carbon methyl signals were shifted sufficiently from the protons at C_2 and C_5, to which they are spin coupled, to show up as clear doublets. The values for coupling constants quoted in Table VII were obtained from these spectra. A slight variation of the coupling constant with concentration ratio (shift reagent/substrate) may reflect small disturbances of conformational equilibria by the shift reagent.

In the proton spectrum of (*E,Z/Z,E*)-1-acetoxy-1,2,5-trimethyl-1-silacyclopentane (3) the carbon methyl groups,



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Me_2 and Me_5, which appear as one broad doublet at 1.05 ppm, are affected to a considerably different extent by the addition of $Eu(fod)_3$. One, taken to be Me_5, was shifted, at a molar concentration ratio (shift reagent/substrate) of 0.42, downfield by 1.43 ppm, while the other, Me_2, was shifted by only 0.82 ppm. On the other hand, while H-2 experienced a significant downfield shift of ~2.1 ppm, H-5 was affected to a smaller extent (~1.0 ppm). Consequently, Me_2 (δ 1.87), which is coupled to H-2 (δ 3.2; $\Delta\delta/J$ = 21.0), appeared as an equal-intensity doublet, while Me_5 (δ 2.48), being coupled to H-5 (δ 2.1; $\Delta\delta/J$ = 5.6), showed a marked "roof effect" with an intensity ratio of 2:1.

The proton spectra of isomers A and C were examined in the presence of $Eu(fod)_3$ in an analogous way. The effect of shift reagent on the methyl groups of isomer A resembled closely the behavior of Me_5 in the *E,Z/Z,E* isomer. At a molar concentration ratio (shift reagent/substrate) of 0.42 the methyl groups appeared at δ 2.65, 1.66 ppm downfield from their position in the spectrum of the uncomplexed compound, as a doublet of unequal intensity (~2:1), due to the close resonance position of H-2. In contrast, the methyl groups of isomer C appeared at δ 1.70, only 0.70 ppm downfield from their position in the original spectrum, as a doublet of equal intensity (molar concentration ratio of shift reagent/substrate was 0.45). A was therefore identified as the *Z,Z* and C as the *E,E* isomer, which confirms identification based on silicon methyl chemical shifts. Displacement of chloride in 1-chloro-1,2,5-trimethyl-1-silacyclopentane by acetate thus takes place with predominant (~90%) inversion of configuration at silicon.

Isomerization of 1-Acetoxy-1,2,5-trimethyl-1-silacyclopentane. (i) Attempts to induce isomerization by trifluoroacetic acid failed. Instead, the formation of a new compound, presumably 1-(trifluoroacetoxy)-1,2,5-trimethyl-1-silacyclopentane, with inversion of configuration at silicon was indicated by NMR, although this compound was not isolated. Thus, from a *Z,Z*:*E,E* = 71:29 mixture of acetates the trifluoroacetate mixture *E,E*:*Z,Z* = 71:29 (by NMR) was formed.

(ii) Tetra-*n*-butylammonium iodide, which caused facile isomerization of 1-chloro-1,2,5-trimethyl-1-silacyclopentane, was found completely inert toward 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane. This may reflect the relative ease of formation of silicenium ion intermediates from two different precursors. Perhaps chloride, being a better leaving group, forms a silicenium ion more easily than does the corresponding acetate.

(iii) Sodium methoxide yielded fully isomerized 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane within a few hours, depending on its concentration. The kinetics of this reaction were followed by measuring the ratio of peak heights of *E,E* and *Z,Z* silicon methyl signals, which are well separated, in the proton NMR spectrum. The isomer ratio at equilibrium was found to be *Z,Z*:*E,E* = 24:76. The equilibration showed the logarithmic time dependence, arising from first-order kinetics for the interconversion of the isomers, and the data were processed as described above for the chloro derivative (individual rate constants are given in the Experimental Section). An approximately linear relationship between the rate of isomerization and the concentration of sodium methoxide was found to hold up to a concentration of about 8×10^{-3} M, giving second-order rate constants of ca. 1×10^{-2} M^{-1} s^{-1} for the *Z,Z* → *E,E* reaction and ca. 3×10^{-3} M^{-1} s^{-1} for the *E,E* → *Z,Z* reaction. At higher concentrations of sodium methoxide the rates increased only slightly due to the limited solubility of sodium methoxide in the chloroform/methanol mixture.

The ease of isomerization of 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane by sodium methoxide and, in contrast, the ineffectiveness of tetra-*n*-butylammonium iodide point to a mechanism different from the one postulated for the isomerization of the corresponding chloride.

A possible explanation is that, unlike iodide, methoxide can reversibly form a pentacoordinated silicon species which can undergo pseudorotation. Alternatively, methoxide may displace acetate which then brings about racemization by S_N2-Si displacements on 1-acetoxy-1,2,5-trimethyl-1-silacyclopentane.

Mass Spectra. The mass spectra of all derivatives described showed fragmentation patterns corresponding to the loss of one molecule of propene (M - 42) and then an allyl radical (M - 82) or another molecule of propene (M - 84), or, alternatively, one molecule of methylcyclopropane (M - 56) as described previously.[1] Stereochemical differences are lost early in the fragmentation sequence so that no useful differences between isomers could be observed.

Experimental Section

Proton NMR spectra were determined on JEOL JNM-MH-100 and JEOL JNM-PS-100 instruments (100 MHz) and at the National NMR Centre, Canberra, Australia (270 MHz); ^{13}C NMR spectra were determined on a JEOL JNM-FX-100 instrument (25 MHz) and at the National NMR Centre (68 MHz). All spectra were run in $CDCl_3$ solutions with Me_4Si or $CHCl_3$ as internal standard. A Varian Aerograph 200 GC instrument with a SGE GSB/SE 30/S SGOT glass capillary column (minimum effective plate number of 20 000) was used to check the purity of reaction products and to determine their isomeric composition. Mass spectra were recorded at 70 eV on an MS902S spectrometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne, and the Microanalytical Unit, University of Queensland.

1-Chloro-1,2,5-trimethyl-1-silacyclopentane. Method (a): with Triphenylmethyl Chloride. A solution of 1,2,5-trimethyl-1-silacyclopentane (1.28 g, 0.01 mol), of isomeric composition *E,E*:*E,Z*/*Z,E*:*Z,Z* = 37:63:0, was stirred with trityl chloride (2.78 g, 0.01 mol) in refluxing benzene (50 mL) for 4 h. The solvent was removed under reduced pressure to a volume of ~5 mL. Triphenylmethane was removed by filtration from the cooled solution. The residue gave, by distillation, the title compound (0.7 g, 43%). Its isomeric composition was, by ^1H NMR (270 MHz) and GC, *Z,Z*:*E,Z*/*Z,E*:*E,E* = 24:63:13.

Method (b): with Benzoyl Peroxide/Carbon Tetrachloride. A solution of 1,2,5-trimethyl-1-silacyclopentane (4.0 g, 25 mM) in carbon tetrachloride (150 mL) was heated to reflux with catalytic amounts of benzoyl peroxide. The reaction was followed by ^1H NMR. The silicon methyl resonances of the reaction products appeared ~0.4 ppm downfield from those of the starting material. The rate of conversion remained constant throughout the experiment and depended only on the concentration of the initiator. The reaction was complete after ~16 h. A higher boiling product was also formed whose structure is discussed elsewhere.[11] Removal of the solvent under reduced pressure and distillation yielded the title compound (3.9 g, 77%), bp 106–110 °C (100 mm). The mass spectrum of the isomeric mixture showed the following peaks: *m/e* (rel intensity) 164 (14), 162 (39), 122 (36), 120 (100), 105 (44), 78 (72). The retention times for the *E,Z*/*Z,E*, *Z,Z*, and *E,E* isomers on analytical GC were 9.9, 10.3, and 10.8 min, respectively, at 80 °C and 80 mmHg.

Anal. Calcd for $C_7H_{15}SiCl$: C, 51.7; H, 9.3; Cl, 21.8. Found: C, 50.7; H, 9.3; Cl, 21.6.

Isomerization of 1-Chloro-1,2,5-trimethyl-1-silacyclopentane. To a solution of 1-chloro-1,2,5-trimethyl-1-silacyclopentane (*E,E*:*E,Z*/*Z,E*:*Z,Z* = 80:2:18; 2 mg in 200 μL of CS_2, 0.61×10^{-1} M) were added 0.5, 1, 2, 5, 10, and 20 μL of a 0.302 M solution of tetra-*n*-butylammonium iodide in acetone to give concentrations of 7.6×10^{-4}, 1.5×10^{-3}, 3.0×10^{-3}, 7.4×10^{-3}, 1.44×10^{-2}, and 2.74×10^{-2} M, respectively. The change of isomeric composition from *E,E*:*E,Z*/*Z,E*:*Z,Z* = 80:2:18 to the equilibrium composition of 44:2:54 was followed by GC; the k (k') values were found to be 7.9×10^{-5} (6.4×10^{-5}), 2.0×10^{-5} (1.6×10^{-4}), 2.6×10^{-4} (2.1×10^{-4}), 5.4×10^{-4} (4.4×10^{-4}), and 11.0×10^{-4} (9.0×10^{-4}), s^{-1}, respectively. k and k' for 2.74×10^{-2} M of tetra-*n*-butylammonium iodide could not be determined with accuracy by GC, because isomerization was essentially complete within 20 min.

1-Methoxy-1,2,5-trimethyl-1-silacyclopentane. To a solution of 1-chloro-1,2,5-trimethyl-1-silacyclopentane (2 g, 12.3 mM) in dry ether (25 mL) was added sodium methoxide (12.4 mM) in methanol (6 mL), and the mixture stirred for $^1/_2$ h. Salts were removed by filtration. The residue gave, by distillation, the title compound (1.2 g, 62%), bp 94–96 °C (100 mm). Mass spectrum: *m/e* (rel intensity), 158 (51), 143 (20), 115 (100), 114 (27), 102 (41), 101 (56), 91 (26), 75 (73), 74 (77), 59 (63). Retention times on GC at 80 °C and 80 mmHg were 9.0 and 10.1 min, respectively.

Anal. Calcd for $C_8H_{18}SiO$: C, 60.7; H, 11.5. Found: C, 60.7; H, 11.4.

1-Fluoro-1,2,5-trimethyl-1-silacyclopentane. Method (a): with Boron Trifluoride. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (0.9 g, 5.6×10^{-3} mol) was refluxed with boron trifluoride etherate (1 g, 7.1×10^{-3} mol) in dry ether (10 mL) for 24 h. After removal of solvent, the residue was taken up in hexane and the BF_3 removed. The residue gave, by distillation, the title compound (0.4 g, 49%), bp 55–60 °C (80 mm).

Method (b): with Silver Fluoride. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (0.6 g, 3.7×10^{-3} mol) was stirred with silver fluoride (1.0 g, 7.9×10^{-3} mol) in dry ether (5 mL) for 2 h. Solid material was removed by filtration and washed with ether. The filtrate gave, by distillation, the title compound (0.3 g, 55%), bp 58–60 °C (80 mm).

Method (c): with Tetra-*n*-butylammonium Fluoride. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (1.6 g, 10^{-2} mol) was stirred with tetra-*n*-butylammonium fluoride (5 g, 1.9×10^{-2} mol) in carbon disulfide or ether (50 mL). The progress of the reaction was followed by GC. The *Z,Z* and *E,Z*/*Z,E* isomers had identical retention times on SE30, but the concentration of the *Z,Z* isomer was determined by substracting the known concentration of *E,Z*/*Z,E* isomer. After 24 h of stirring at room temperature the conversion was approximately 50%. Another 16 h at reflux temperature was necessary to complete the reaction. Salts were removed by filtration. The filtrate yielded, by distillation, the title compound (0.9 g, 62%), bp 76–78 °C (120 mm).

The identity of the products obtained by the three methods was shown by their ^1H NMR and mass spectra and by their identical retention times on GC. The mass spectra showed the following peaks: *m/e* (rel intensity) 146 (54), 105 (28), 104 (100), 89 (99), 79 (80), 63 (35), 55 (33), 47 (24). ^{19}F spectra were measured with trifluoroacetic acid on external lock.

Anal. Calcd for $C_7H_{15}SiF$: C, 57.5; H, 10.3; F, 13.0. Found: C, 57.3; H, 10.0; F, 12.9.

1-Acetoxy-1,2,5-trimethyl-1-silacyclopentane. 1-Chloro-1,2,5-trimethyl-1-silacyclopentane (1.0 g, 6.2×10^{-3} mol) was stirred in dry ether (25 mL) with solid silver acetate (1.5 g, 9.0×10^{-3} mol) at room temperature. The reaction was completed in ~24 h, as shown by GC. Salts were removed by filtration and washed with ether. The filtrate gave, by distillation, the title compound (0.7 g, 61%), bp 67–69 °C (10 mm). The mass spectrum of the isomeric mixture showed the following peaks: *m/e* (rel intensity) 186 (26), 171 (22), 144 (22), 143 (74), 129 (19), 103 (40), 102 (100), 101 (22), 87 (13), 75 (12), 74 (13), 61 (40).

Anal. Calcd for $C_9H_{18}SiO$: C, 58.0; H, 9.7. Found: C, 56.8; H, 97.

The mass spectrum, corresponding to bis(1,2,5-trimethylsilacyclopentyl) ether, gave the following peaks: *m/e* (rel intensity) 270 (73), 255 (28), 228 (30), 187 (85), 166 (39), 151 (100), 145 (40), 124 (31), 119 (25), 95 (27).

Lanthanide-Induced Shifts. Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)Eu(III) ($Eu(FOD)_3$) was sublimed before use. $CDCl_3$ contained some $CHCl_3$ for internal reference. The concentration of the substrate was kept constant, only the concentrations of $Eu(FOD)_3$ being varied. The initial sample was prepared by dissolving ~70 mg of $Eu(FOD)_3$ in 500 μL of a solution of substrate in $CDCl_3$ (~60 mg/mL). This was the sample with the highest ratio of shift reagent to substrate. Successive samples were then prepared by adding aliquots of substrate solution.

Isomerization of 1-Acetoxy-1,2,5-trimethyl-1-silacyclopentane. (a) By Trifluoroacetic Acid. The title compound (40 mg, 0.22 mM; *Z,Z*:*E,E* = 71:29) was dissolved in $CDCl_3$ (0.5 mL) and trifluoroacetic acid (30 mg, 0.26 mM) added. The reaction was followed by NMR. While the silicon methyl signal at 0.23 ppm (*E,E* isomer) decreased gradually, a new signal at 0.50 ppm appeared. The singlet at 0.36 ppm remained unchanged. After 4 h at room temperature the signal at 0.23 ppm had disappeared almost completely. The ratio of isomers (peak

(11) F. Franke and P. R. Wells, *Tetrahedron Lett.*, in press.

heights at 0.36 and 0.50 ppm) was again 71:29.

(b) By Sodium Methoxide. The title compound (40 mg, 0.22 mM; *Z,Z*:*E,E* = 65:35) was dissolved in $CDCl_3$ (0.5 mL). 1, 2, 5, 10, and 20 μL of a 0.81 M sodium methoxide solution in methanol were added. Relative amounts of isomers were determined by measuring the peak heights of their silicon methyl signals. $k'(k)$ values, in s^{-1}, were found to be 1.77×10^{-5} (5.62×10^{-6}) for [NaOMe] = 1.63×10^{-3} M, 2.91×10^{-5} (9.23×10^{-6}) for [NaOMe] = 3.25×10^{-3} M, 5.32×10^{-5} (1.68×10^{-5}) for [NaOMe] = 8.07×10^{-3} M, 5.83×10^{-5} (1.84×10^{-5}) for [NaOMe] = 1.60×10^{-2} M, and 6.21×10^{-5} (1.95×10^{-5}) for [NaOMe] = 3.13×10^{-2} M.

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Registry No. 1, 71518-75-7; (*E,E*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71518-76-8; (*E,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-07-3; (*Z,Z*)-1-chloro-1,2,5-trimethyl-1-silacyclopentane, 71564-08-4; (*E,E*)-1-methoxy-1,2,5-trimethyl-1-silacyclopentane, 71518-77-9; (*E,Z*)-1-methoxy-1,2,5-trimethyl-1-silacyclopentane, 71564-09-5; (*Z,Z*)-1-methoxy-1,2,5-trimethyl-1-silacyclopentane, 71564-10-8; (*E,E*)-1-fluoro-1,2,5-trimethyl-1-silacyclopentane, 71564-11-9; (*E,Z*)-1-fluoro-1,2,5-trimethyl-1-silacyclopentane, 71564-12-0; (*E,E*)-1-acetoxy-1,2,5-trimethyl-1-silacyclopentane, 71605-99-7; (*E,Z*)-1-acetoxy-1,2,5-trimethyl-1-silacyclopentane, 71606-00-3; (*Z,Z*)-1-acetoxy-1,2,5-trimethyl-1-silacyclopentane, 71518-78-0; (*E,E*)-1,2,5-trimethyl-1-silacyclopentane, 68212-43-1; (*E,Z*)-1,2,5-trimethyl-1-silacyclopentane, 71564-13-1; sodium methoxide, 124-41-4.

Facile Synthesis of 6,7-Dichloro-1-oxo-5-indanylalkanoic Acids and Related Compounds via Triflate Displacement

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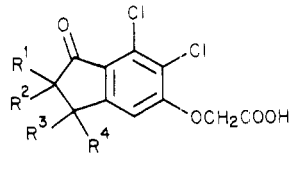
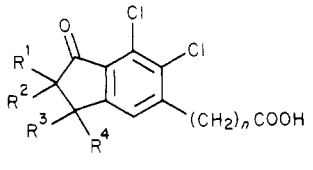
Substitution of the triflate group in 6,7-dichloro-1-oxo-5-indanyl trifluoromethanesulfonates, by a conjugative addition–displacement mechanism, provides a new route to 1-indanones with a variety of substituents in the 5-position.

A number of compounds from the 6,7-dichloro-1-oxo-5-indanyloxyacetic acid series (**1**) possess interesting pharmacological activities. The diuretic and uricosuric properties of some members of this series have been described,[1] and more recently, biological activities of potential therapeutic value have been found in other compounds of the series.[2]



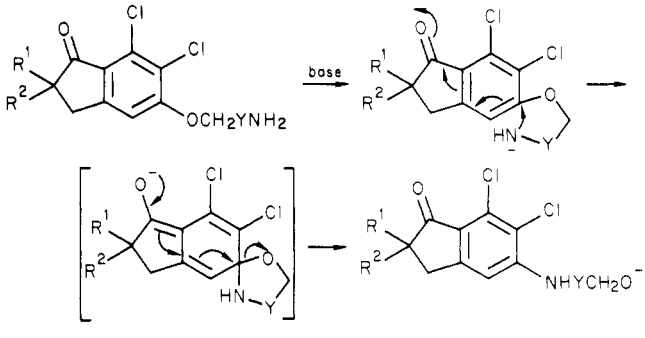
1



2

To the medicinal chemist the related series of compounds lacking the ether linkage between the aromatic ring and the side chain (**2**) is of interest as a component in the structure/activity pattern in this area, but hitherto only arduous methods of synthesis for compounds in this second series have been available. A new approach to this problem was suggested by the observation that the ether linkage in derivatives of compounds of general formula **1** could be substituted by a nitrogen under strongly basic conditions.[3] This rearrangement presumably takes place via a conjugative addition–displacement mechanism as outlined in Scheme I, and finds a parallel in a recent publication.[4]

Scheme I



Y = CH_2 or CO

The first idea of exploiting the unusual reactivity of this system for the preparation of compounds of formula **2** was to try to bring about the intramolecular displacement of the 5-oxygen by a carbanion. Several possible O-derivatives could be envisaged as candidates for this type of rearrangement. However, before we embarked on this

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(2) Unpublished work in our laboratories

(3) H. W. R. Williams and O. W. Woltersdorf, Jr., unpublished results.

(4) R. Bayles, M. C. Johnson, R. F. Maisey, and R. W. Turner, *Synthesis*, 31, 33 (1977).

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